



DECLARATION

I, Isolde U. Wasley, hereby declare:

that I am familiar with the English and German languages, am a professional translator from German into English and am employed as a translator in the office of VENABLE LLP, 575 7th Street, N.W., Washington, DC 20004-1601;

That I have read the attached translation and hereby state that this translation is a true and accurate translation of the German priority application text for United States Patent Application No. 10/552,165, filed on October 11, 2005 (inventor: Udo STEFFL), said translation thereof being attached hereto and made a part of this declaration.

To the best of my knowledge and belief, the above translation is accurate and fairly reflects the contents and meaning of the original document.

I declare under the penalty of perjury under the laws of the United States of America that the foregoing is true and correct.

Executed on November 16, 2006

Isolde U. Wasley
Isolde U. Wasley

Polyolefin Tube

5

The present invention relates to a silane cross-linked, chlorine-resistant polyolefin tube made by the so-called single-stage silane process.

10 Plastic tubular conduits are made from a large number of polymer materials.

In the field of materials for thermoplastic tubes particularly polyvinyl chloride, polypropylene, polyethylene, polybutylene or cross-linked polyolefin are
15 utilized.

The cross-linking of polyolefins may be effected chemically or physically. As described, for example, in Kautschuk, Gummi, Kunststoff, 34th year, No. 3/1981, pages 197 ff, in
20 the technically significant cross-linking technologies a distinction is made between radiation cross-linking, peroxide cross-linking and silane cross-linking.

The last-named process distinguishes itself from the other
25 cross-linking methods primarily by the process technique: In a first process step the polymer chain radicals are generated with the aid of the usual radical initiators, to which, in a second process step, the silane molecules with their vinyl function are added. Such silane-grafted
30 polymers may still be thermoplastically processed. The

cross-linking proper takes places after shaping by a silane condensation reaction in the presence of heat and moisture. Such a so-called two-stage silane process is described in United States Patent No. 3,646,155.

5

In contrast, British Patent No. 1,526,398 describes the so-called single-stage silane process. In this process all additives are simultaneously dosed with the polymer in a specially designed extruder for producing online the
10 desired extruded material. Subsequently, cross-linking is effected in the presence of heat and moisture.

An application of a single-stage silane process, particularly for drinking-water tubes in the USA, is
15 described in United States Patent No. 6,284,178. In this process a residual methanol content of less than 12.2 ppm in the tube is obtained by using a maximum of 1.8 weight percent mixture of silane/peroxide/catalyst and by setting the duration of cross-linking at more than 4 hours. No
20 mention is made concerning a chlorine-resistant provision of such a silane cross-linked polyethylene tube with special stabilizers. Rather, the combination of Irganox B215 and Irganox 1010 described in United States Patent No. 6,284,178 has - because of the low melting point of the
25 phenolic constituents - a much too low extraction resistance against chlorine water.

This prevents in practice the use of silane tubes made in accordance with United States Patent No. 6,284,178.

The reason is that drinking water in the USA is provided,
30 for purposes of disinfection, with a larger chlorine dose as compared to European conditions. As known by the specialist, at an appropriate pH-value, chlorine water may

produce hypochlorous acid HOCl which is strongly oxidizing and therefore may lead to a premature failure of the tube.

It is the object of the invention to provide a silane
5 cross-linked polyolefin tube which is made in a one-stage process and which is chlorine-resistant at a chlorine content between 0.1 and 5 ppm, which has minimum degree of cross-linking of 60%, and which further satisfies the standard specifications for cross-linked polyethylene
10 tubes, set by the various ASTM and NSF norms.

The above object has been successfully achieved according to the invention by a tube having a polyolefin composition, comprising:

- 15 (A) a polyolefin,
(B) a mixture of an organic silane of the general formula RSiX_3 with a radical-generating constituent and a catalyst, and with
(C) a stabilizer mixture of a high-molecular phenolic
20 constituent with a sulfur-containing constituent, a phosphorus-containing processing stabilizer and a metal deactivator.

It has been a main difficulty in solving the object of the
25 invention that the added stabilizers and the radical-generating constituents mutually affect one another in the reactive extrusion process, and thus, after processing, negatively alter the terminal cross-linking degree and the residual stabilization in the tube. The level of residual
30 stabilization, however, is decisive for a good chlorine resistance and is achieved only by a deliberate choice of the type and quantity of the individual constituents.

Furthermore, the possible extraction of the stabilizer package in chlorine water is critical. A suitable resistance to extraction may be achieved only if the phenolic constituent combines a large molecular weight with a high melting point and the sulfur-containing constituent, the phosphorus-containing processing stabilizer and the metal deactivator have large non-polar partial chains.

The degree of crystallinity of the cross-linked tube is, not in the least, also an important magnitude; it is essential for the durability of its service life. This is so, because, as a rule, the degree of crystallinity of the utilized polyethylene (PE) is reduced, for example, from 70% to, for example, 65% by the graft reaction and cross-linking, so that measures have to be taken to raise the degree of crystallinity to the value appropriate for its application in question. This is achieved according to the invention by a tempering step at temperatures between 70-95°C. The duration required therefor depends from the PE utilized, how the reaction is run, and the specification to be obtained.

In the description that follows, the invention will be set forth in more detail.

The constituent (A) of the silane cross-linked polyolefin tube according to the invention is contained at 100 weight parts in the recipe and is either a low-pressure polyethylene (HDPE) made according to the Ziegler process or the Phillips process and having a degree of crystallinity between 60 and 80% and a density of from

0.942 to 0.965 g/cm³ or a polyethylene of medium density (MDPE; 0.930 to 0.942 g/cm³).

The constituent (B) is a mixture of an organic silane of the general formula RSiX₃ (B1), a radical-generating constituent (B2) and a catalyst (B3). The organic silane RSiX₃ (B1) may be a vinyltrimethoxysilane, vinyltriethoxysilane or 3-

(methacryloxy)propyltrimethoxysilane. The radical-

generating constituent (B2) may be an alkylperoxide, acylperoxide, ketoneperoxide, hydroperoxide, peroxocarbonate, perester, peroxoketal, peroxooligomer or an azo compound. Particularly preferred are organic alkylperoxides having half-value times of 0.1 hour at temperatures > 80°C, such as 2,5-dimethyl-2,5-di(tertiary-butylperoxy)hexane and/or 2,5-dimethyl-2,5-di(tertiary-butylperoxy)3-hexine and/or di(tertiarybutyl)peroxide and/or 1,3-di(tertiary-butyl-peroxyiso-propyl)benzol and/or dicumylperoxide and/or tertiary-butylcumylperoxide. The catalyst (B3) may be dibutyltindilaurate, dibutyltinoxide, tinooctoate, dibutyltinmaleate or titanylacetate. The weight part of the constituent (B), related to constituent (A), may be between 0.1 and 5 parts; particularly preferred are weight parts between 1 and 3.

Constituent (C) is a stabilizer mixture of a high-molecular phenolic constituent (C1) having a high melting point, a sulfur-containing constituent (C2), a phosphorus-containing processing stabilizer (C3) and a metal deactivator (C4).

The high-molecular phenolic stabilizer (C1) having a high melting point is selected from the group of 2,2'-methylene-

bis(6-tertiary-butyl-4-methylphenol), 1,3,5-trimethyl-
2,4,6-tris(3,5-di-tertiary-butyl-4-hydroxybenzyl)benzol,
octadecyl 3-(3,5-di-tertiary-butyl-4-
hydroxyphenyl)propionate, 1,1,3-tris(2-methyl-4-hydroxy-5-
5 tertiary-butylphenyl)butane, tris(3,5-di-tertiary-butyl-4-
hydroxybenzyl)isocyanurate, tris(4-tertiary-butyl-3-hdroxy-
2,6-dimethylbenzyl)isocyanurate, pentaerythritol
tetrakis(3,5-di-tertiary-butyl-4-hydroxyhydrocinnamate) or
1,3,5-tris(3,5-di-tertiary-butyl-4-hydroxybenzyl)triazine.

10

The sulfur-containing constituent (C2) may be a 5-tertiary-
butyl-4-hydroxy-2-methylphenyl sulfide, 3-tertiary-butyl-2-
hydroxy-5-methylphenyl sulfide, dioctadecyl-3,3'-
thiodipropionate, dilauryl 3,3'-thiodipropionate or
15 ditetradecyl-3,3'-thiodipropionate.

15

The phosphorus-containing processing stabilizer (C3) may be
a tris(nonylphenyl)phosphite, tris(2,4-di-tertiary-
butylphenyl) phosphite, tetrakis(2,4-di-tertiary-
20 butylphenyl)-4,4'-biphenyldiphosphonite, 3,9-
bis(octadecyloxy)-2,4,8,10-tetraoxa-3,9-
diphosphaspiro[5.5]undecan or 3,9-bis(2,4-dicumylphenoxy)-
2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecan.

20

25 The metal deactivator (C4) is selected from the group of
1,2-bis(3,5-di-tertiary-butyl-4-
hydroxyhydrocinnamoyl)hydrazide or 2,2'-oxalyldiamidobis-
(ethyl-3-(3,5-di-tertiary-butyl-4-hydroxyphenyl)propionate)
or oxalic bis(benzylidenehydrazide).

30

Very particularly preferred constituents (C) are 1,3,5-
trimethyl-2,4,6-tris(3,5-di-tertiary-butyl-4-

hydroxybenzyl)benzol (C1), dioctadecyl-3,3'-thiodipropionate (C2), tris(2,4-di-tertiary-butylphenyl)phosphite (C3) and 1,2-bis(3,5-di-tertiary-butyl-4-hydroxyhydrocinnamoyl)hydrazide (C4).

5

The weight part of the constituent (C) related to the constituent (A) may be between 0.1 and 5 parts.

To the chlorine-resistant tubes according to the invention
10 there may be added up to 20 weight parts additives, related to constituent (A), in the form of up to 5 weight parts lubricant or processing agents, up to 5 weight parts nucleation agents, up to 5 weight parts antistatic agents, up to 10 weight parts process oils, up to 10 weight parts
15 pigments, up to 5 weight parts expanding agents or up to 5 weight parts ultraviolet stabilizers.

By virtue of these particularities, the making of silane cross-linked, chlorine-resistant tubes according to the
20 single-stage process is not obvious. Only the deliberate selection of the type and quantity of special stabilizers and the recipe adapted thereto as well as the process technique permit not only the manufacture of tubes having the usual property image, but also lead in a surprising
25 manner to an advantageous property image, as set forth in the formulation of the object of the invention, particularly as concerns the resistance against a chlorine content between 0.1 and 5 ppm.

30 The chlorine-resistant, silane cross-linked polyolefin tubes are made according to the single-stage silane process, that is, the graft reaction of the silane of the

constituent (B1) on the polyolefin of the constituent (A) and the shaping proceed simultaneously in one process step. Additionally to the monosil process described in the state of the art, a barrier screw is utilized for an effective
5 distribution of the liquid constituents prior to the grafting step and for avoiding a preliminary cross-linking. A fusion pump may additionally also be utilized.

After processing, the tubes are cross-linked in a cross-linking chamber in a water vapor atmosphere at temperatures
10 between 80 and 100°C until a cross-linking degree of more than 60% is obtained. Thereafter occasionally a tempering step at 70-95°C follows, until the desired, application-dependent degree of chrystallinity is obtained.

15 Tests on service life durability after a tempering step show, because of the increased degree of chrystallinity, an increased service life of the chlorine-resistant tubes according to the invention.

20 The application of the cross-linked tubes according to the invention is preferably in the field of tubes for drinking water and/or water for industrial use with and without a diffusion blocking layer.

25 The invention will be further explained by way of exemplary embodiments whose description follows.

The compositions are given in weight parts related to 100 weight parts of constituent (A) and are present in the

30 Examples as follows:

Examples

	Example 1	Example 2	Example 3	Example 4
polyethylene constituent (A)	100 [1]	100 [2]	100 [2]	100 [1]
constituent (B)	2.30 [3]	2.05 [3]	2.10 [3]	2.30 [3]
constituent (C)	0.41 (C1) [4] 0.10 (C2) [6] 0.16 (C3) [8] 0.10 (C4) [9]	0.49 (C1) [4] 0.15 (C2) [6] 0.19 (C3) [8] 0.12 (C4) [9]	0.53 (C1) [4] 0.16 (C2) [6] 0.21 (C3) [8] 0.13 (C4) [9]	0.41 (C1) [4] 0.10 (C1) [5] 0.10 (C2) [6] 0.16 (C3) [8] 0.10 (C4) [9]

	Example 5	Example 6	comparison example
polyethylene constituent (A)	100 [1]	100 [1]	100 [2]
constituent (B)	2.30 [3]	2.30 [3]	1.95 [3]
constituent (C)	0.41 (C1) [4] 0.10 (C2) [7] 0.16 (C3) [8] 0.10 (C4) [9]	0.41 (C1) [4] 0.10 (C2) [6] 0.10 (C4) [9]	[10]

5 Explanations [1] to [10] for constituents (A), (B), (C1) to (C4) for the Examples:

- [1] polyethylene having a density [g/cm³] of 0.952 and MFI [g/10min] of 5-7 (190°C/2.16kg)
- [2] polyethylene having a density [g/cm³] of 0.944 and MFI
10 [g/10min] of 4 (190°C/2.16 kg)
- [3] silane/peroxide/catalyst mixture: viscosity [mPasec] = 2.5 (at 23°C); density [g/cm³] = 0.969, colorless liquid
- [4] 1,3,5-trimethyl-2,4,6-tris(3,5-di-tertiary-butyl-4-
15 hydroxybenzyl)benzol; molecular weight [g/mol] = 775
- [5] pentaerythritol tetrakis(3,5-di-tertiary-butyl-4-hydroxyhydrocinnamat); molecular weight [g/mol] = 1178
- [6] dioctadecyl-3,3'-thiodipropionate; molecular weight [g/mol] = 683

- [7] 3-tertiary-butyl-2-hydroxy-5-methylphenyl sulfide;
molecular weight [g/mol] = 358.5
- [8] tris(2,4-di-tertiary-butylphenyl)phosphite; molecular
weight [g/mol] = 647
- 5 [9] 1,2-bis(3,5-di-tertiary-butyl-4-
hydroxyhydrocinnamoyl)hydrazide; molecular weight
[g/mol] = 552
- [10] stabilizer-MB: Vibatan PEX Antiox 02012, added
quantity 5 parts.

10

Examples 1-6:

In a single-screw extruder which is provided with a barrier
screw and a metering device and which is intended for the
liquid silane/peroxide/catalyst mixture, the polyolefin (A)
15 and the stabilizer mixture (C) are dosed by means of a
metering scale. The mixture is melted and the liquid
silane/peroxide/catalyst mixture (B) is dosed in and shaped
to form a tube.

20 The requirements concerning a chlorine-resistant drinking-
water tube in the USA are listed in the NSF Protocol P171
(1999 edition). A combination of a "Differential Scanning
Calometry" (DSC) experiment with a modified test for
service life durability has been found suitable for a
25 practical determination of the chlorine resistance.

With the DSC experiment, oxidation reactions of synthetic
materials may be generally determined. The OIT (oxidizing
induction time) represents a process with which information
30 may be obtained concerning the stability of polyolefin
tubes against oxidizing attacks. In the static process
(ASTM norm D3895) utilized here, the specimen is heated to

a temperature of 210°C in an inert atmosphere. The temperature is maintained. After equilibrium sets in, the scavenging gas is switched from an inert atmosphere to an oxidizing atmosphere. The exothermal oxidizing reaction then starts after a certain delay. By means of the DSC experiments fine nuances in the critical residual stabilizer content may be detected in the chlorine-resistant, silane cross-linked polyolefin tubes of the invention.

10

Further, a modified test for service life durability has been performed as a pre-test. In this test the tube sections having a length greater than 30 cm are exposed under pressure to chlorinated tap water at a PH-value of 7 and submitted to a test of service life durability at temperatures of 20°C, 95°C and 110°C and subjected to different pressures p [Nmm⁻²]. Every 8 days the tube sections are taken out and examined concerning the chlorine concentration and PH-value.

15

The table below shows the properties of the tubes according to the invention.

20

	Example 1	Example 2	Example 3	Example 4
mean cross-linking degree in [%] according to ASTM F876-01	71.2	72.6	74.6	70.6
OIT 210°C [min]	73.3	105.7	119.3	91.0
service life at 95°C in hours p=4.65-4.71*) with chlorine water	>1660	>1660	>1660	>1660
service life at 110°C in hours p=2.75-2.81*) with chlorine water	>380	>380	>380	>380
service life at 20°C in hours p=12.0-12.5*) with chlorine water	>290	17.5	12.95	>290

	Example 5	Example 6	comparative example
mean cross-linking degree in [%] according to ASTM F876-01	66.7	68.8	65.5
OIT 210°C [min]	80.0	74.4	41.9
service life at 95°C in hours p=4.65-4.77*) with chlorine water	>1660	>1660	0.52
service life at 110°C in hours p=2.75-2.84*) with chlorine water	>380	>380	>380
service life at 20°C in hours p=12.0-12.5*) with chlorine water	>290	290.3	5.33

*) p means the pressure range in Nmm^{-2}

Patent Claims

1. Silane cross-linked polyolefin tubes which are
5 intended for drinking water and/or water for
industrial use, which are resistant to a chlorine
content between 0.1 and 5 ppm, which are made
according to the single-stage process and which have a
minimum cross-linking degree of 60%.
- 10 2. The silane cross-linked polyolefin tubes as defined in
claim 1, characterized in that the polyolefin
composition comprises
(A) a polyolefin,
15 (B) a mixture of an organic silane of the general
formula RSiX_3 with
(B1) a radical-generating constituent (B2) and a
catalyst (B3), and with
(C) a stabilizer mixture of a high melting point,
20 high-molecular phenolic constituent (C1) with a
sulfur-containing constituent (C2), a phosphorus-
containing processing stabilizer (C3) and a metal
deactivator (C4).
- 25 3. The silane cross-linked polyolefin tubes as defined in
claim 2, characterized in that the constituent (A) is
selected from the group of low-pressure polyethylenes
(HDPE) having a degree of crystallinity between 60
and 80% and a density from 0.942 to 0.965 g/cm^3 or a
30 polyethylene having a mean density of 0.930 to 0.942
 g/cm^3 (MDPE).

4. The silane cross-linked polyolefin tubes as defined in claim 2, characterized in that the organic silane of the general formula $\text{RSiX}_3(\text{B1})$ of the constituent (B) is selected from the group of vinyltrimethoxysilane, vinyltriethoxysilane or 3-(methacryloxy)propyltrimethoxysilane.
5. The silane cross-linked polyolefin tubes as defined in claim 2, characterized in that the radical-generating constituent (B2) of the constituent (B) is selected from the group of alkylperoxide, acylperoxide, ketoneperoxide, hydroperoxide, peroxocarbonate, perester, peroxoketal, and/or peroxooligomers, particularly from the group of alkylperoxide.
6. The silane cross-linked polyolefin tubes as defined in claim 2, characterized in that the radical-generating constituent (B2) of the constituent (B) is an azo compound.
7. The silane cross-linked polyolefin tubes as defined in claim 2, characterized in that the radical-generating constituent (B2) of the constituent (B) is an organic alkylperoxide having a half-value time of 0.1 hour at temperatures $> 80^\circ\text{C}$.
8. The silane cross-linked polyolefin tubes as defined in claims 2 and 7, characterized in that the organic alkylperoxide is selected from the group of 2,5-dimethyl-2,5-di(tertiary-butylperoxy)hexane and/or 2,5-dimethyl-2,5-di(tertiary-butylperoxy)3-hexine

and/or di(tertiarybutyl)peroxide and/or 1,3-di(tertiary-butyl-peroxyisopropyl)benzol and/or dicumylperoxide and/or tertiary-butylcumylperoxide.

- 5 9. The silane cross-linked polyolefin tubes as defined in claim 2, characterized in that the catalyst (B3) of the constituent (B) is selected from the group of dibutyltin dilaurate, dibutyltin oxide, tin octoate, dibutyltin maleate or titanium acetate.
- 10 10. The silane cross-linked polyolefin tubes as defined in claim 2, characterized in that the high melting point, high-molecular phenolic constituent (C1) of the constituent (C) is selected from the group of 2,2'-
- 15 methylenebis(6-tertiary-butyl-4-methylphenol), 1,3,5-trimethyl-2,4,6-tris(3,5-di-tertiary-butyl-4-hydroxybenzyl)benzol, octadecyl-3-(3,5-di-tertiary-butyl-4-hydroxyphenyl)propionate, 1,1,3-tris(2-methyl-4-hydroxy-5-tertiary-butylphenyl)butane, tris(3,5-di-
- 20 tertiary-butyl-4-hydroxybenzyl)isocyanurate, tris(4-tertiary-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, pentaerythritol tetrakis(3,5-di-tertiary-butyl-4-hydroxyhydrocinnamate) or 1,3,5-tris(3,5-di-tertiary-
- 25 butyl-4-hydroxybenzyl)triazine.
11. The silane cross-linked polyolefin tubes as defined in claim 2, characterized in that the sulfur-containing constituent (C2) of the constituent (C) is selected
- 30 from the group of 5-tertiary-butyl-4-hydroxy-2-methylphenyl sulfide, 3-tertiary-butyl-2-hydroxy-5-methylphenyl sulfide, dioctadecyl-3,3'-

thiodipropionate, dilauryl-3,3'-thiodipropionate or ditetradecyl-3,3'-thiodipropionate.

12. The silane cross-linked polyolefin tubes as defined in
5 claim 2, characterized in that the phosphorus-
containing processing stabilizer (C3) of the
constituent (C) is selected from the group of
tris(nonylphenyl)phosphite, tris(2,4-di-tertiary-
butylphenyl)phosphite, tetrakis(2,4-di-tertiary-
10 butylphenyl)-4,4'-biphenyldiphosphonite, 3,9-
bis(octadecyloxy)-2,4,8,10-tetraoxa-3,9-
diphosphaspiro[5.5]undecan or 3,9-bis(2,4-
dicumylphenoxy)-2,4,8,10-tetraoxa-3,9-
diphosphaspiro[5.5]undecan.
- 15
13. The silane cross-linked polyolefin tubes as defined in
claim 2, characterized in that the metal deactivator
(C4) of the constituent (C) is selected from the group
of 1,2-bis(3,5-di-tertiary-butyl-4-
20 hydroxyhydrocinnamoyl)hydrazide, or 2,2'-
oxalyldiamidobis-(ethyl-3-(3,5-di-tertiary-butyl-4-
hydroxyphenyl)propionate) or oxalic
bis(benzylidenehydrazide).
- 25
14. The silane cross-linked polyolefin tubes as defined in
claim 2, characterized in that the weight part of
constituent (B), related to constituent (A) is between
0.1 and 5 parts, particularly between 1 and 3 parts.
- 30
15. The silane cross-linked polyolefin tubes as defined in
claim 2, characterized in that the weight part of

constituent (C), related to constituent (A) is between 0.1 and 5 parts.

16. The silane cross-linked polyolefin tubes as defined in
5 claim 2, characterized in that up to 20 weight parts
of additives, related to constituent (A), are added in
the form of up to 5 weight parts of lubricating or
processing agents, up to 5 weight parts of nucleation
agents, up to 5 weight parts of antistatic agents, up
10 to 10 weight parts of processing oils, up to 10 weight
parts of pigments, up to 5 weight parts of expanding
agents or up to 5 weight parts of ultraviolet
stabilizers.
- 15 17. The silane cross-linked polyolefin tubes as defined in
one of the preceding claims, characterized in that the
tube has a cross-linking degree in the range of 60 to
89%, particularly between 65 and 75%.
- 20 18. A method of making a silane cross-linked polyolefin
tube as defined in one of the preceding claims,
characterized in that the graft reaction of the silane
of the constituent (B1) on the polyolefin of the
constituent (A) as well as the shaping proceed
25 simultaneously in the course of one processing step,
while utilizing a barrier screw and/or a fusion pump,
thereafter the tubes are stored in a cross-linking
chamber in a water vapor atmosphere at 80-100°C until
a cross-linking degree in excess of 60% is reached
30 and, lastly, a tempering step occasionally follows at
temperatures between 70 and 95°C until the desired,

application-dependent degree of chrystallinity is reached.

19. Use of the silane cross-linked tubes according to one
5 of the preceding claims for making tubes for drinking
water and/or water for industrial use.

Rehau, April 9, 2003

10 dr.we-zh/e

DC2DOCS1\691155

15